

Structure and Properties of Amorphous LiPON Electrolyte by First-Principles Simulations



TECHNISCHE
UNIVERSITÄT
DARMSTADT

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International Symposium on Electrical Fatigue
in Functional Materials
15-18.9.2014 • Sellin • Rügen • Germany

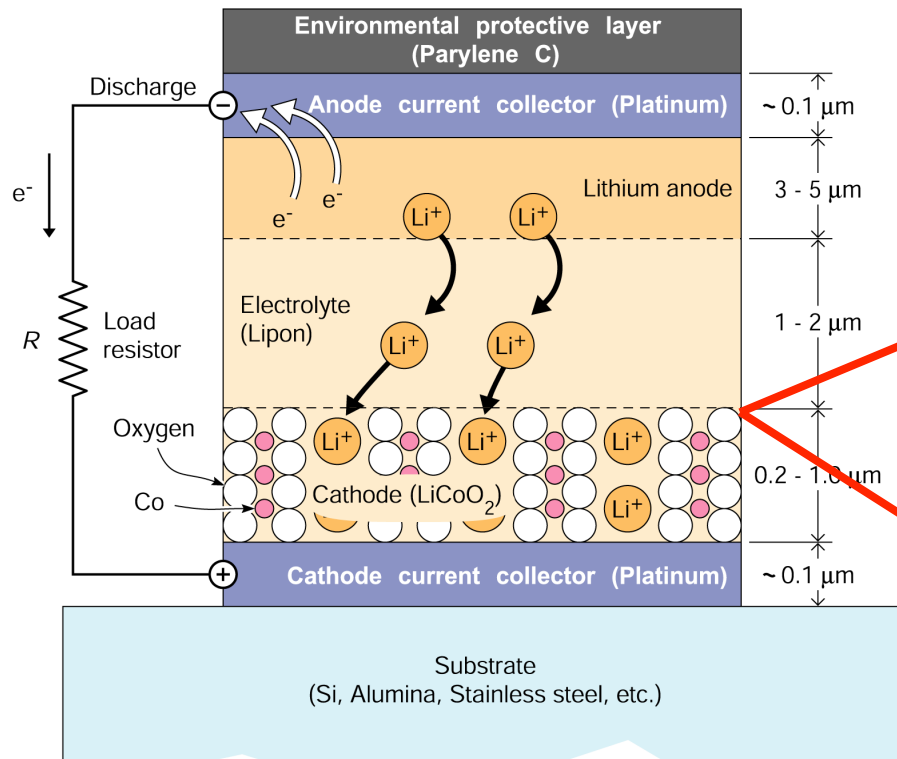
SFB 595

Deutsche
Forschungsgemeinschaft

DFG

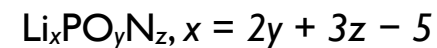


Motivation & goals



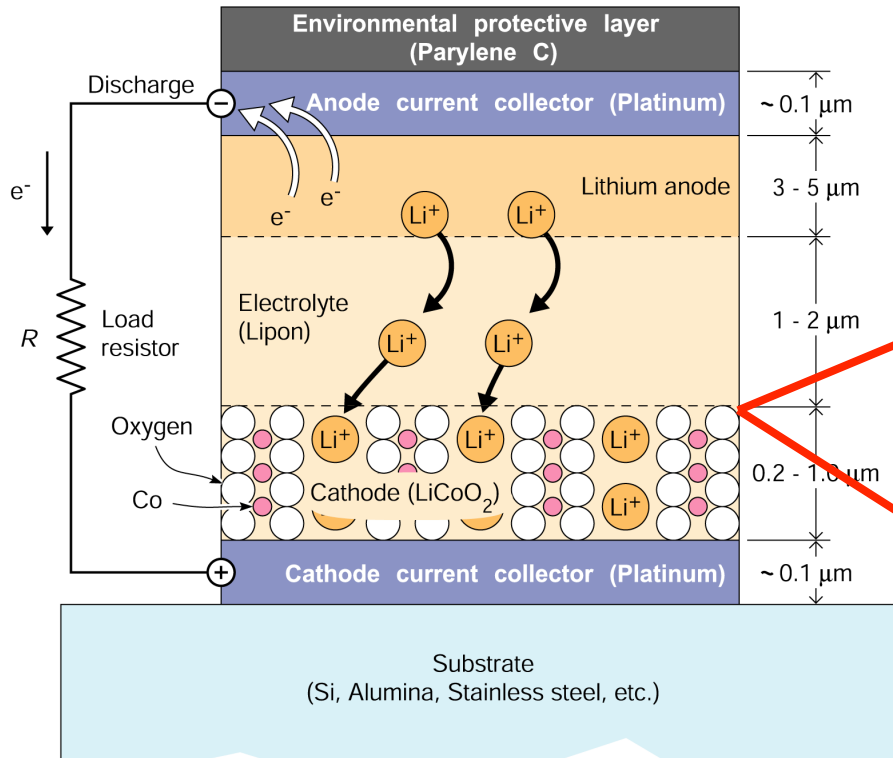
- ▶ solid electrolyte/solid electrode interphases (SESEI) may lead to an increase of the impedance upon cell cycling
- ▶ thin solid-state electrolyte films as stabilizing interfaces

▶ Lithium Phosphorus OxyNitride

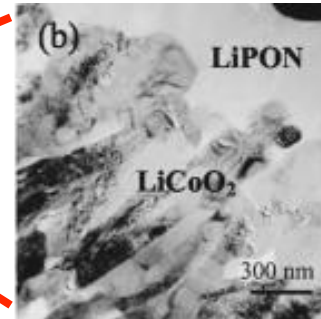


J.B. Bates *et al.*, Oak Ridge National Laboratory

Motivation & goals



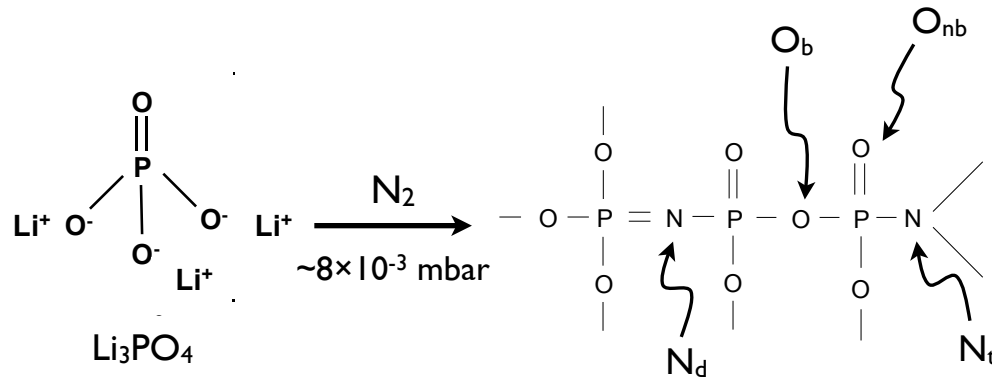
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- ▶ Lithium Phosphorus OxyNitride
 $\text{Li}_x\text{PO}_y\text{N}_z, x = 2y + 3z - 5$
 J.B. Bates et al., Oak Ridge National Laboratory

- ▶ modelling of electrolyte and electrolyte/electrode interfaces/interphases is lacking
 - realistic solid electrolyte glassy structure
 - defectivity
 - interfaces with electrodes
- } understanding battery performance and failure modes

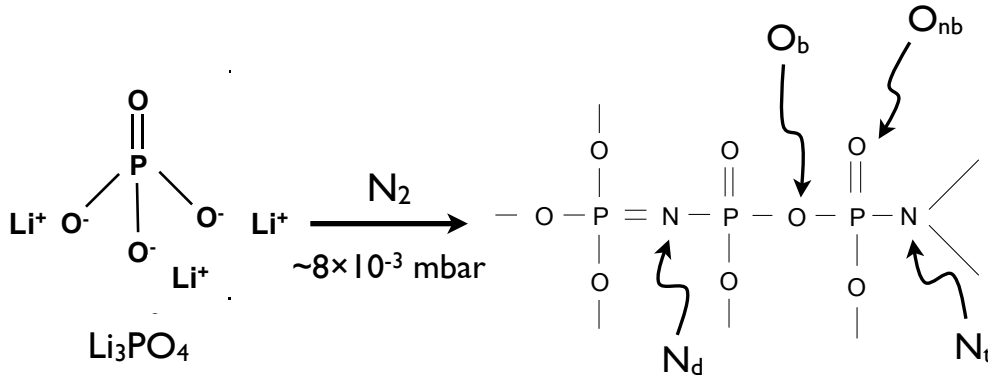
What's LiPON



▶ RF sputtering of Li_3PO_4 in $\text{N}_2 \rightarrow \text{Li}_x\text{PO}_y\text{N}_z$

- bridging O (O_b)
- non-bridging O (O_{nb})
- triply coordinated N (N_t)
- doubly coordinated N (N_d)

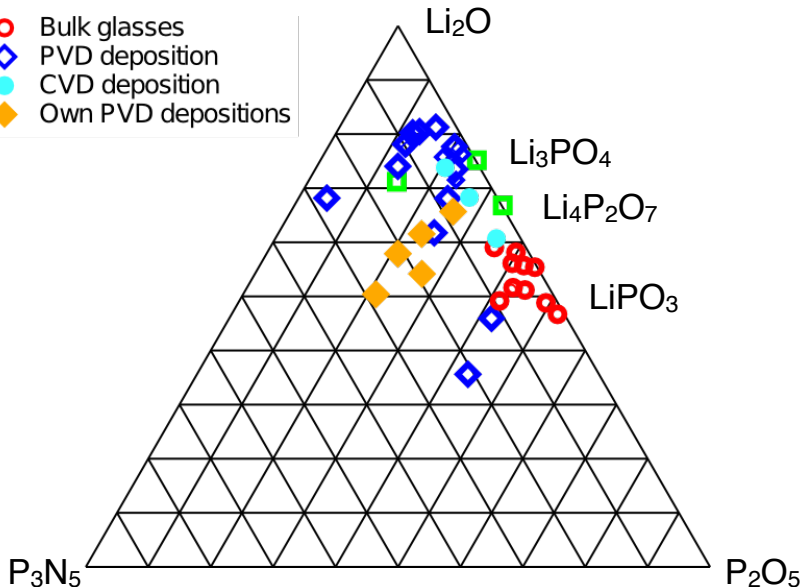
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- Bulk glasses
- ◇ PVD deposition
- CVD deposition
- ◆ Own PVD depositions



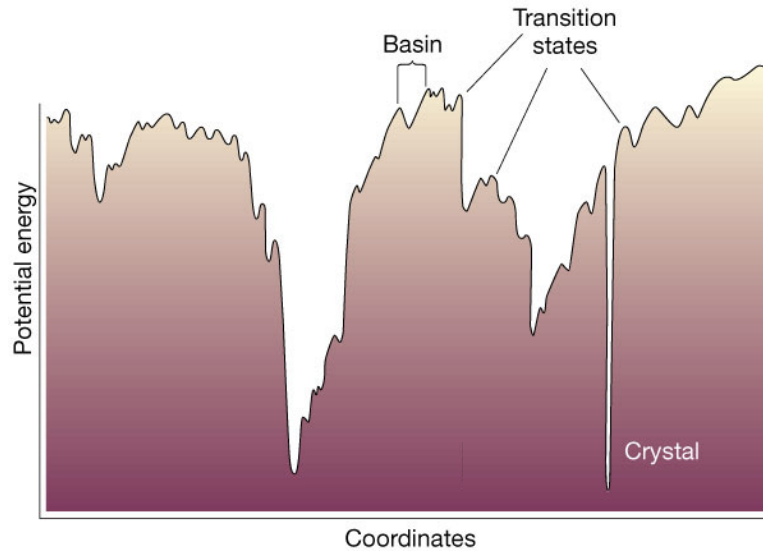
◆ experimental composition:
 $\text{Li}_{1.2}\text{PO}_{2.2}\text{N}_{0.9}$ – non-neutral!

approximant composition(s) needed:

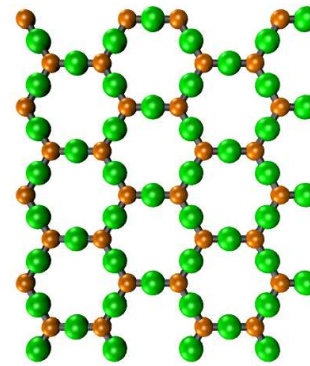
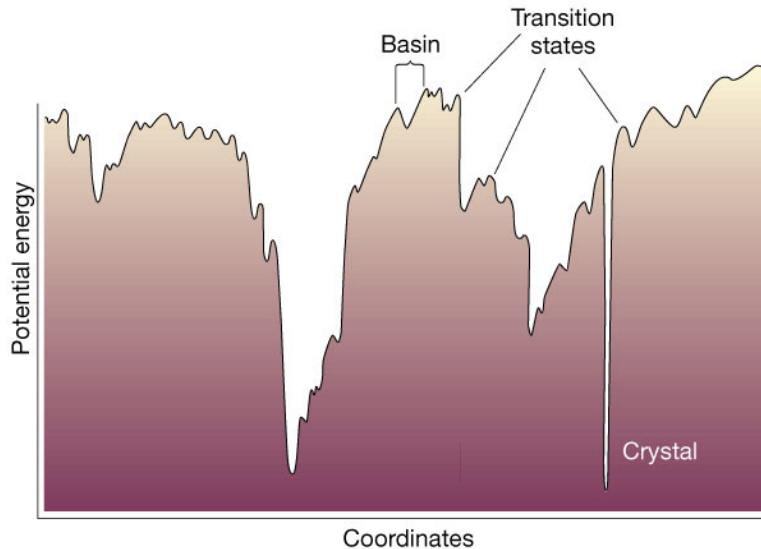
$\text{Li}_{1.25}\text{PO}_2\text{N}_{0.75}$ ($\text{Li}_5\text{P}_4\text{O}_8\text{N}_3$), $\text{Li}_2\text{PO}_2\text{N}$, ...

➔ effect of the composition on the properties of the material (not today)

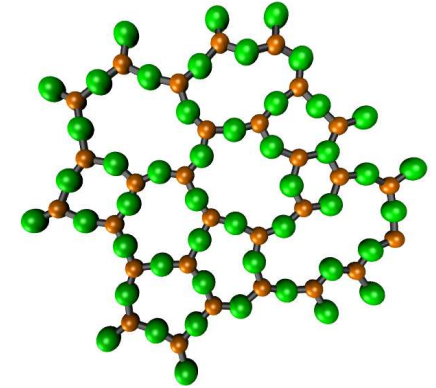
Modelling a glass



Modelling a glass



crystal



glass

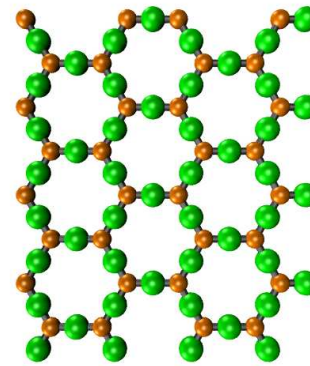
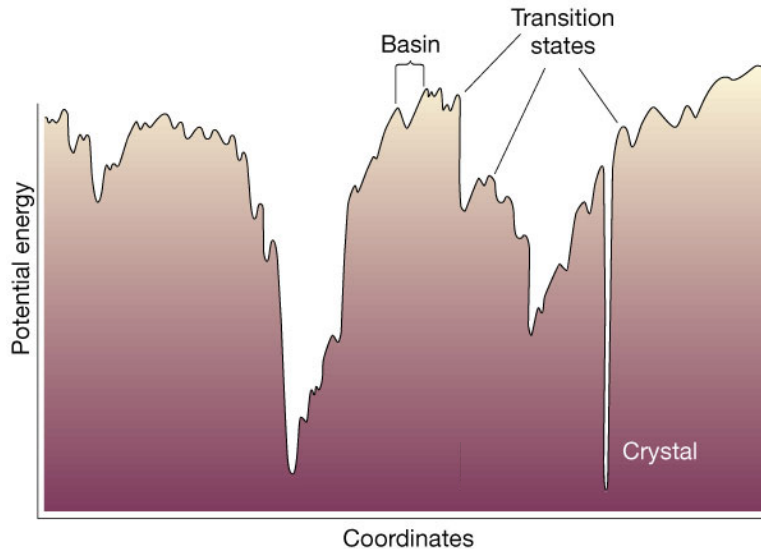
- ▶ glasses and crystals share the same connectivity *within* and *between* local atomic polyhedra (Zachariasen's random network theory)

▶ idea:

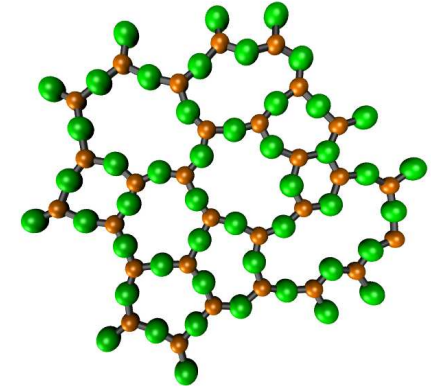
- (let a code) scan the potential energy landscape and identify the most stable structure

➔ evolutionary algorithm

Modelling a glass



crystal



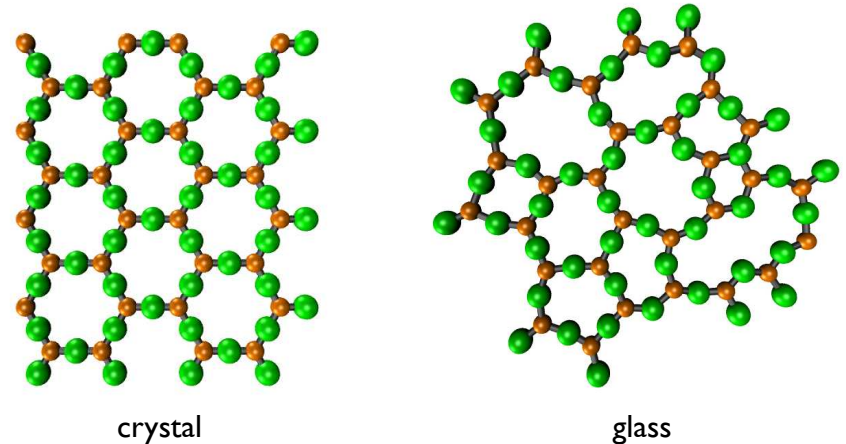
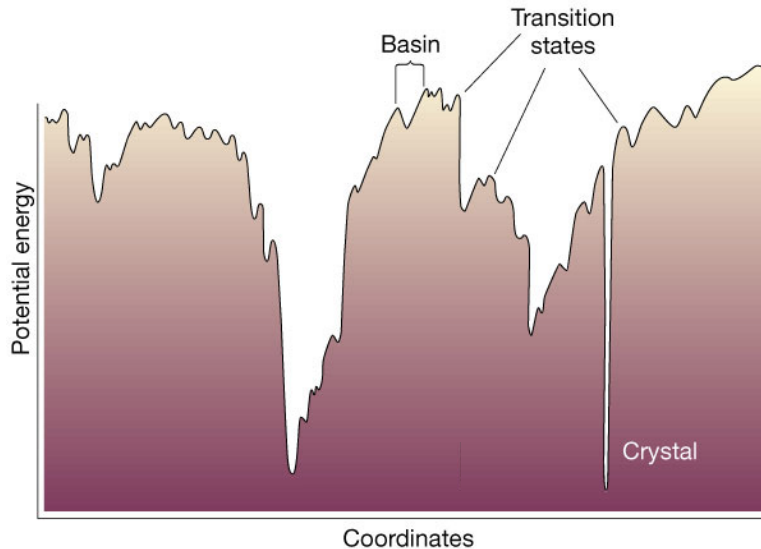
glass

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▶ idea:

- (let a code) scan the potential energy landscape and identify the most stable structure
 - ➔ evolutionary algorithm
- introduce disorder (bond lengths/angles) while keeping connectivity in place
 - ➔ simulated annealing

Modelling a glass



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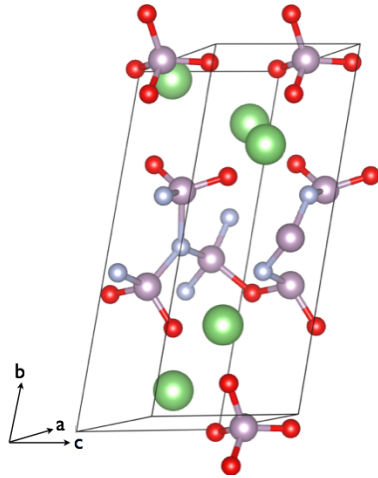
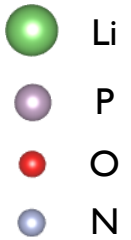
density functional theory

USPEX
Universal Structure Predictor:
Evolutionary Xtallography

+

b-initio
VASP
Vienna
package
simulation

Li₅P₄O₈N₃ – Structure

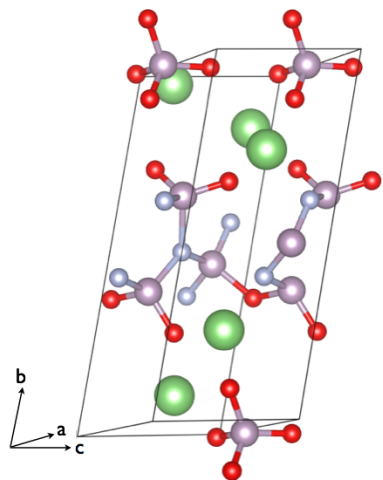
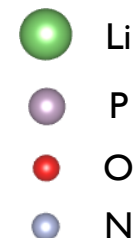


step 1
evolutionary algorithm

$$\frac{N_t}{N_d} = \frac{1}{2} = 0.50$$

$$\frac{O_b}{O_{nb}} = \frac{1}{7} = 0.14$$

Li₅P₄O₈N₃ – Structure

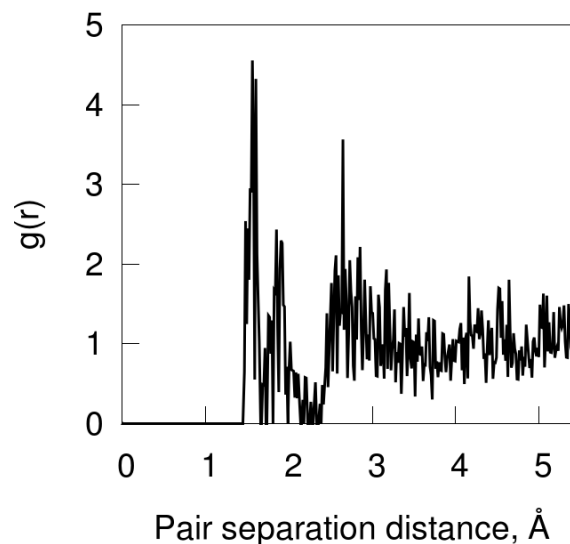
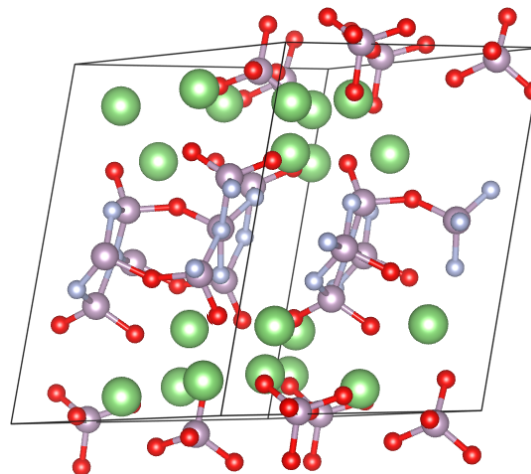


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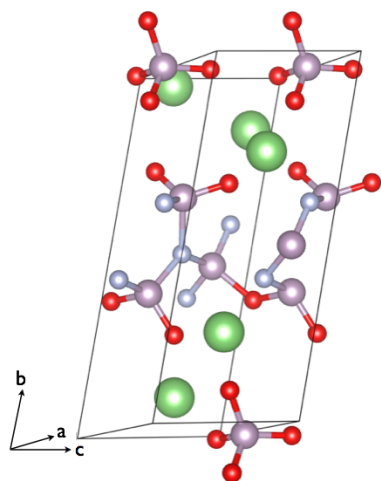
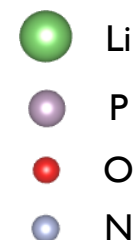
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step 2
4x replication*
+
simulated annealing



*beware of periodic boundary conditions

Li₅P₄O₈N₃ – Structure

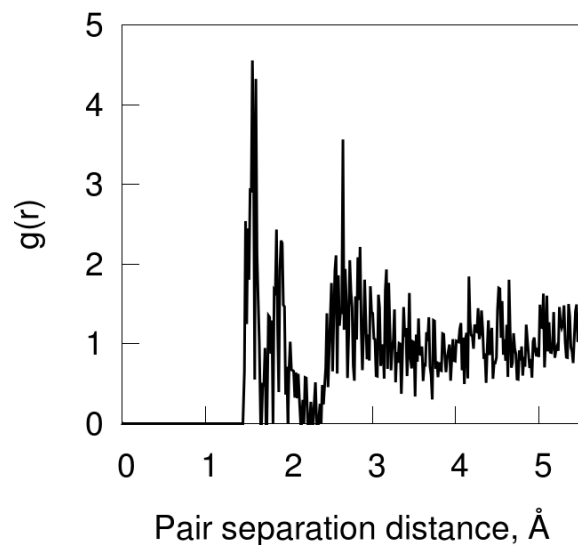
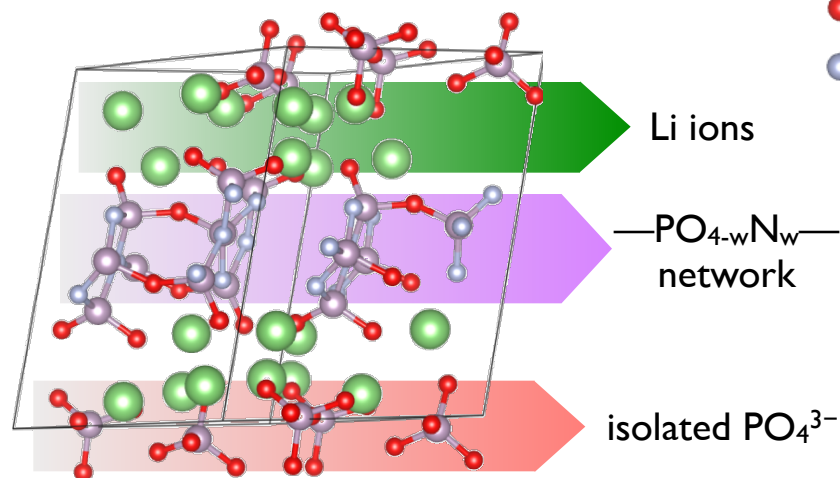


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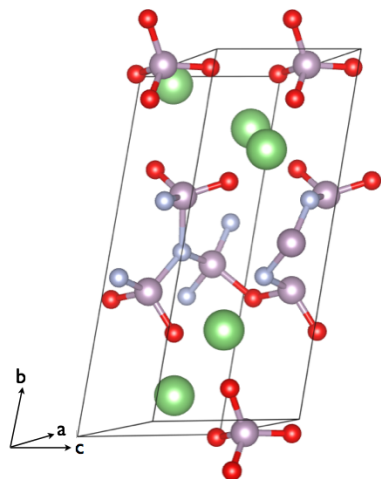
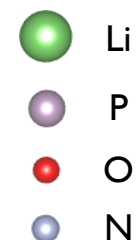
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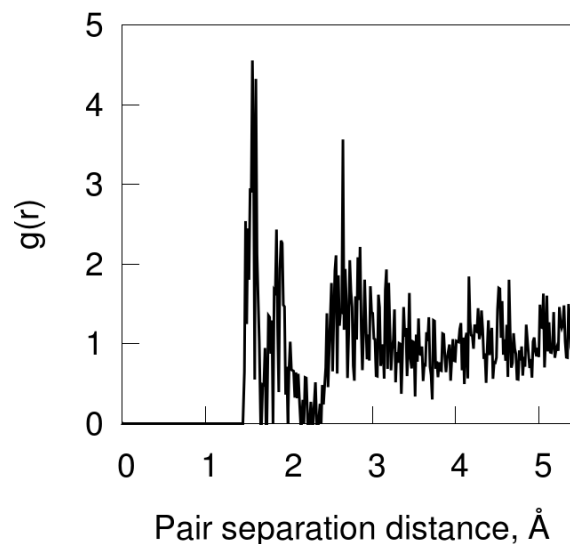
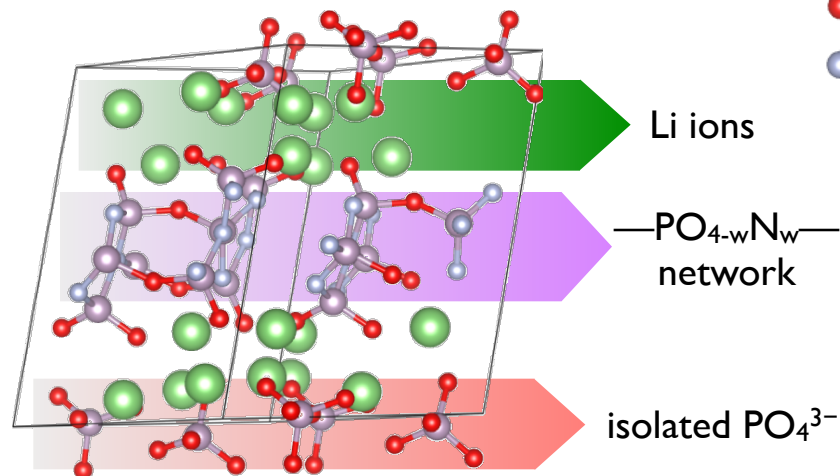


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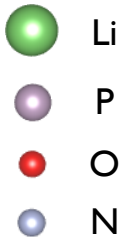
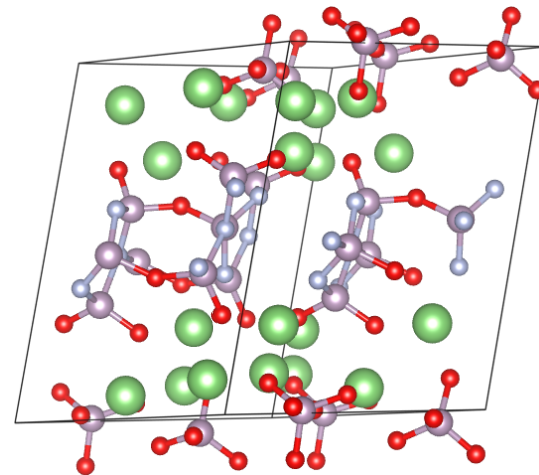


first
computational model of
an amorphous electrolyte
with
non-trivial composition
and cross-linking

*beware of periodic boundary conditions

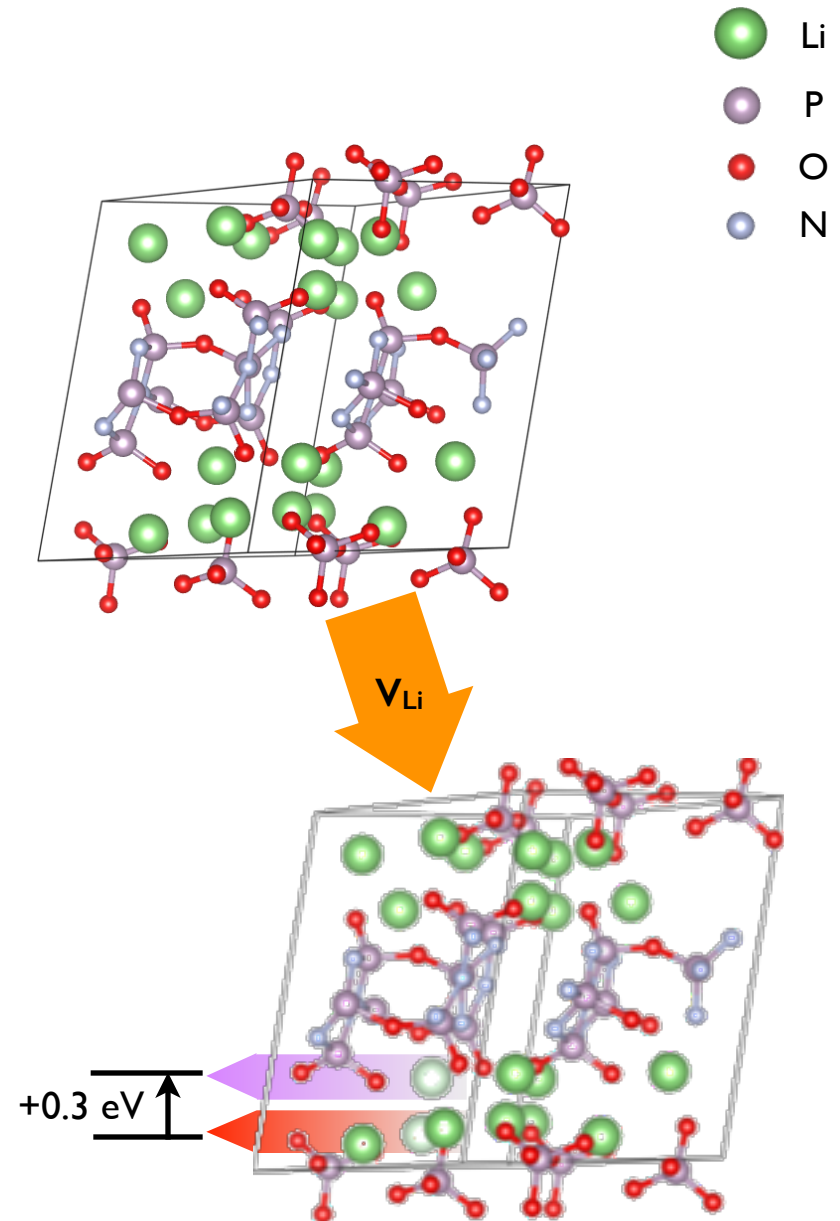
Li₅P₄O₈N₃: defects

- ▶ defectivity (i.e. departure from order) in a disordered material?
- ▶ vacancies and excess interstitials
 - still have to cope with virtually ∞ number of inequivalent sites

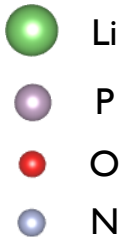


$\text{Li}_5\text{P}_4\text{O}_8\text{N}_3$: defects

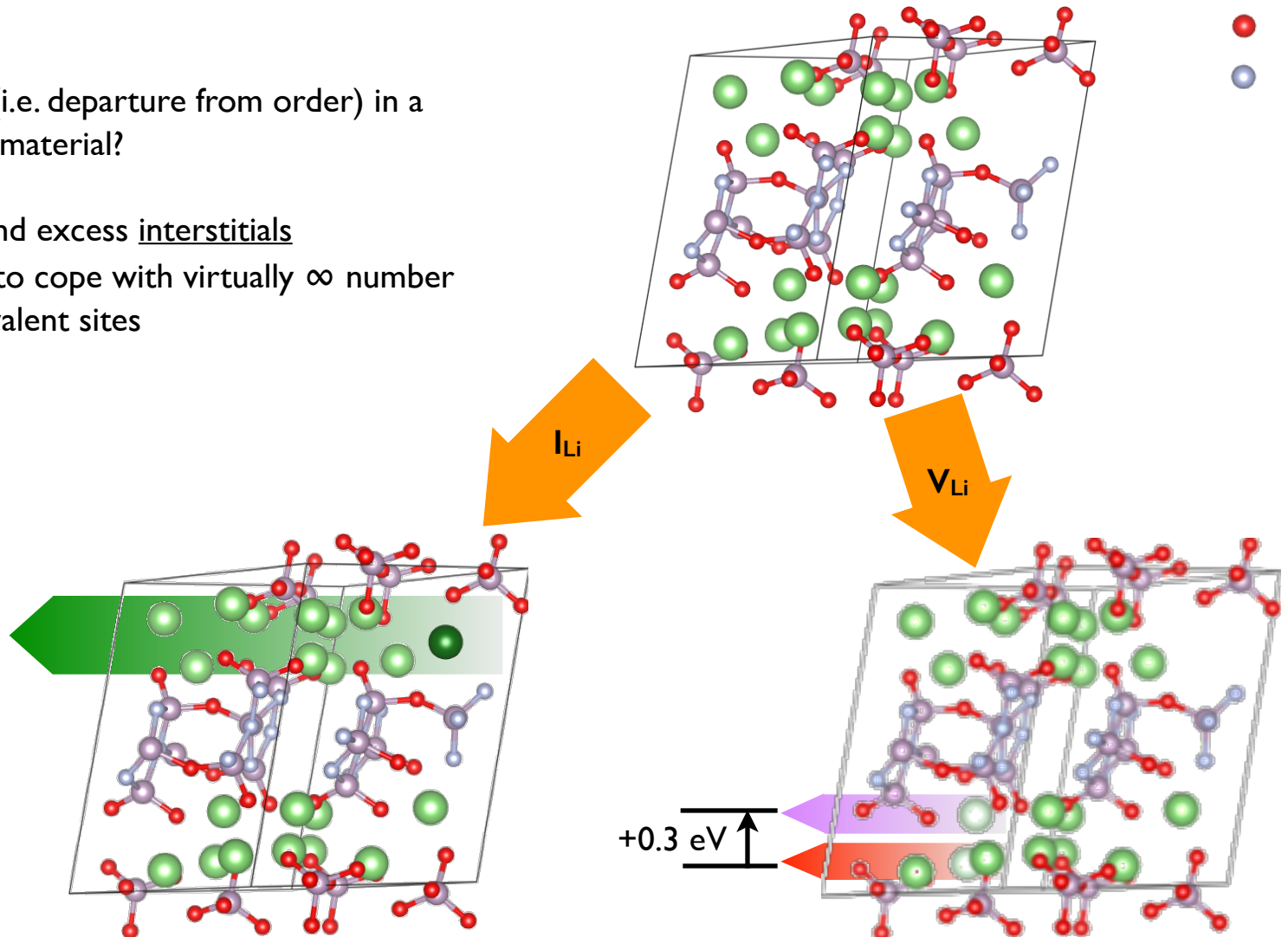
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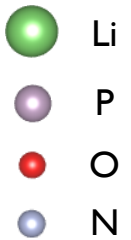
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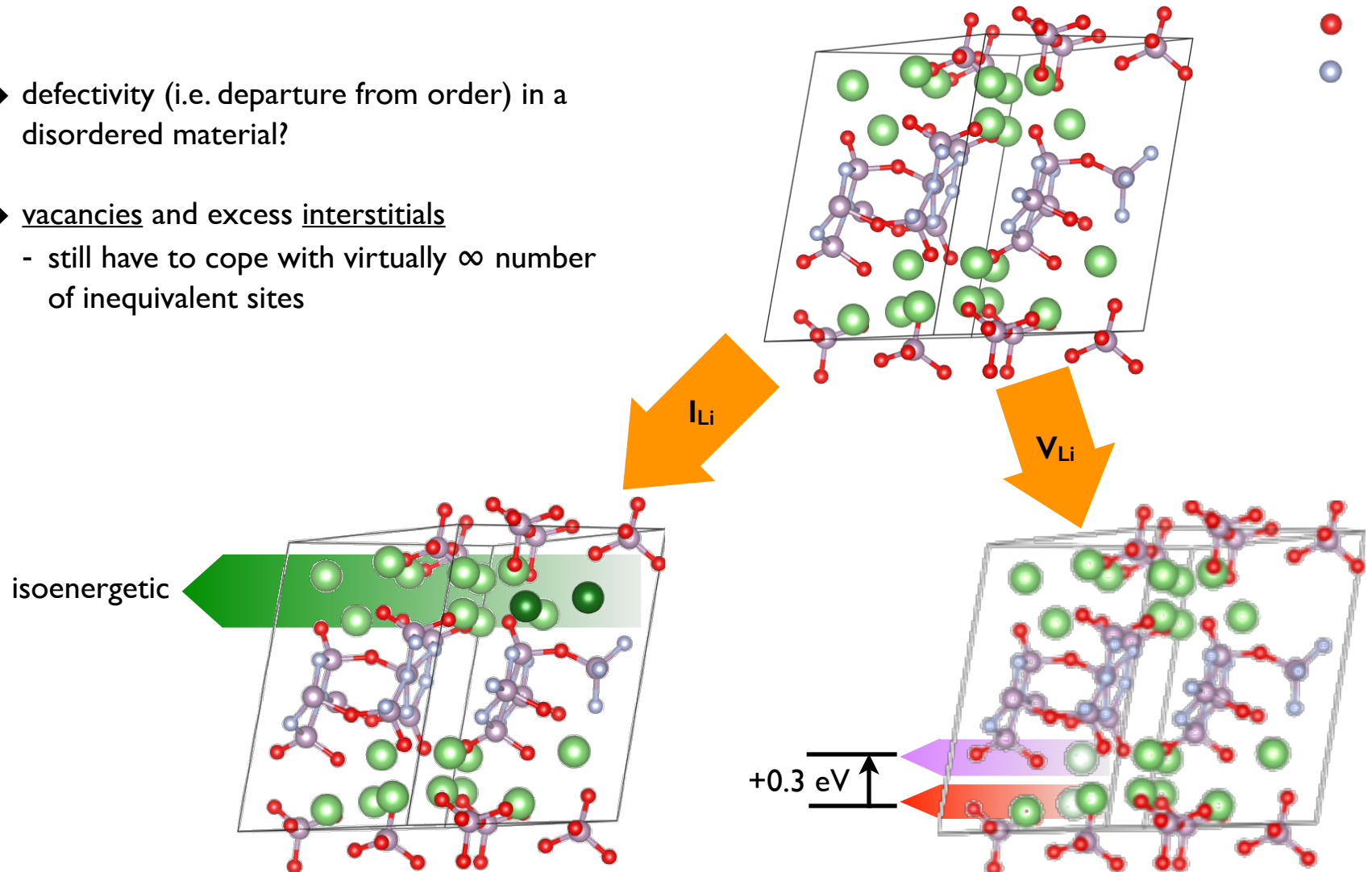
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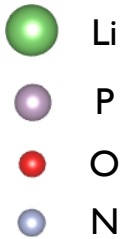
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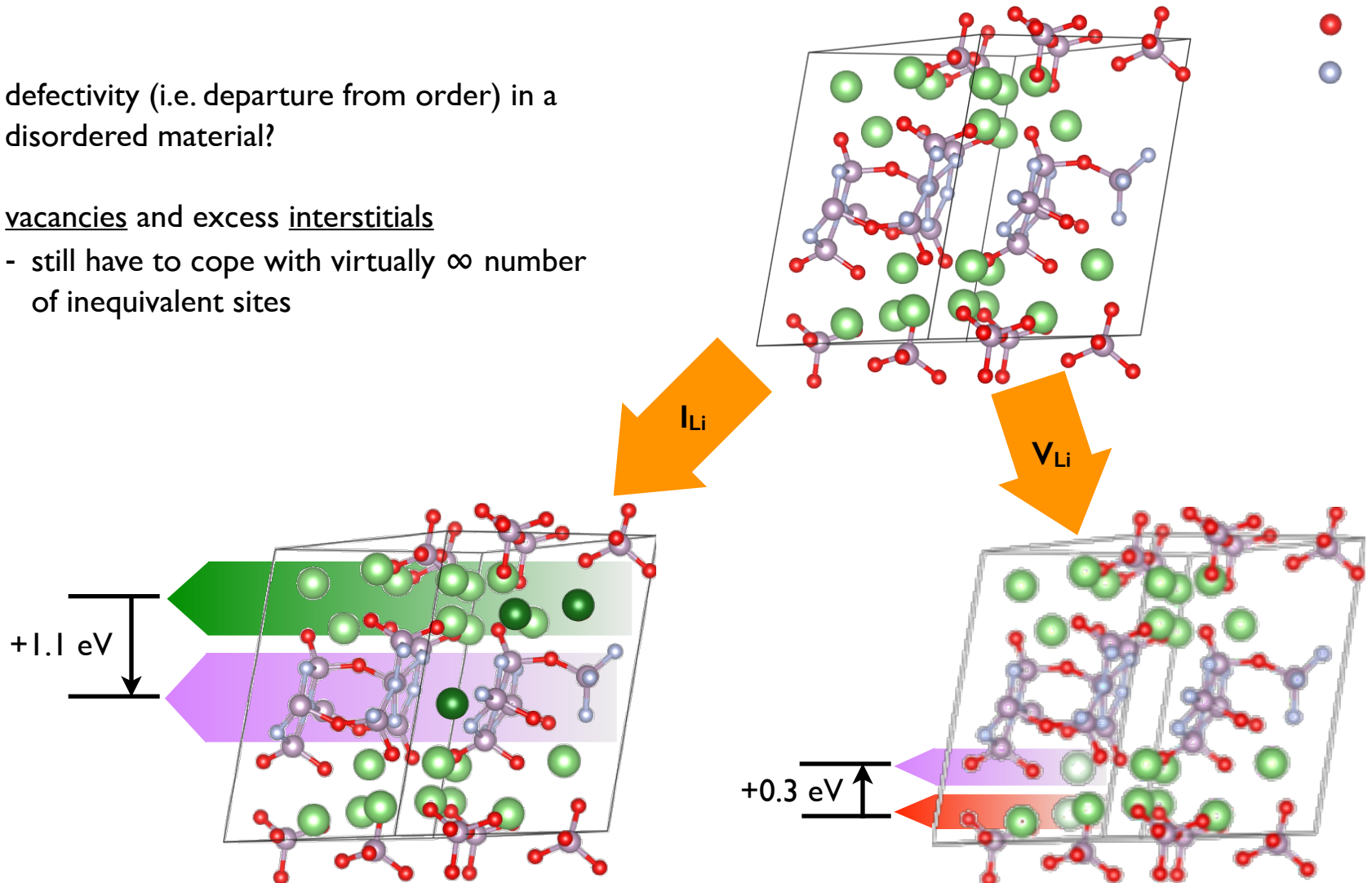
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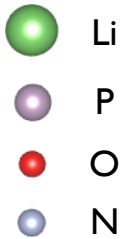
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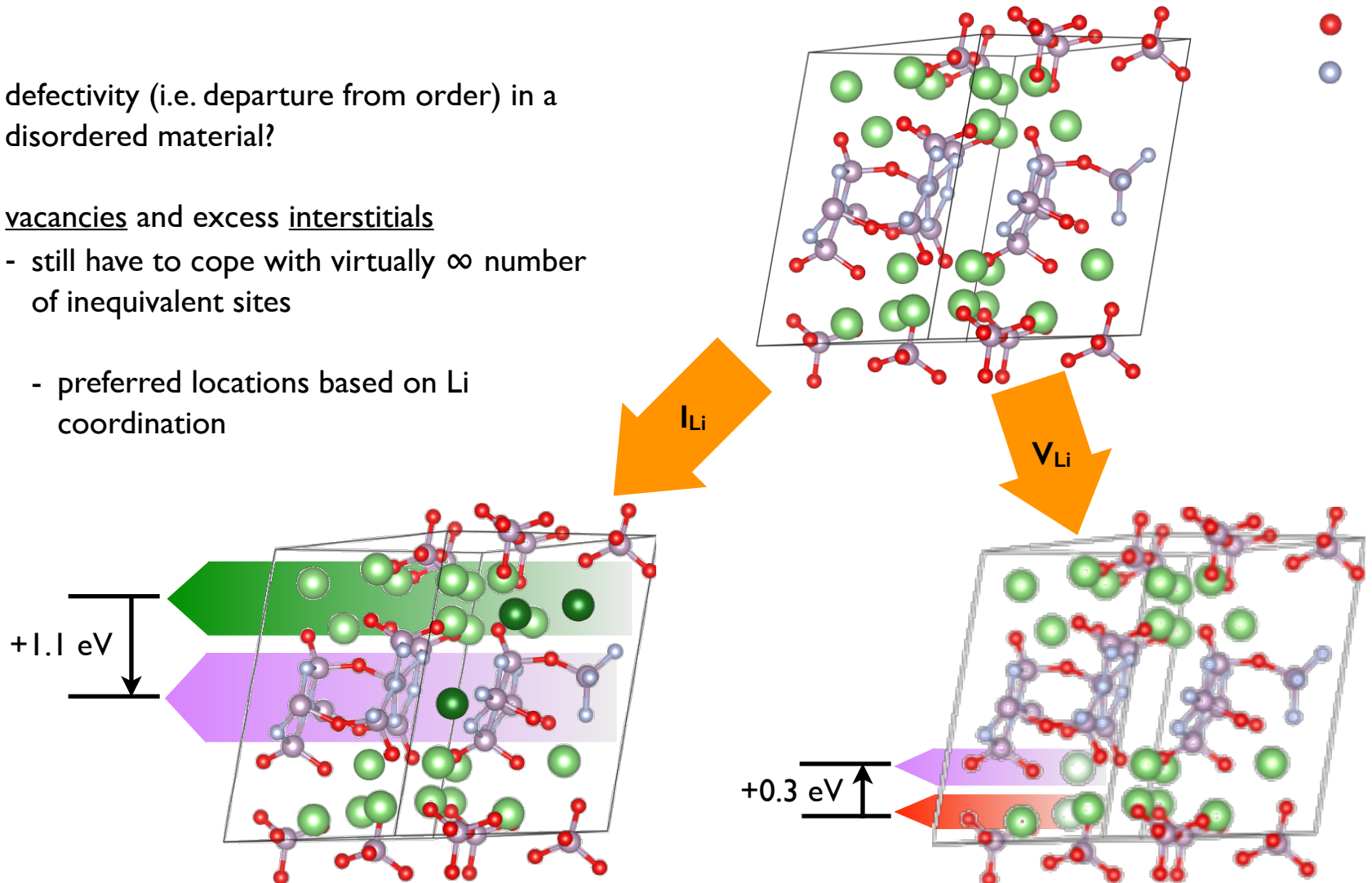
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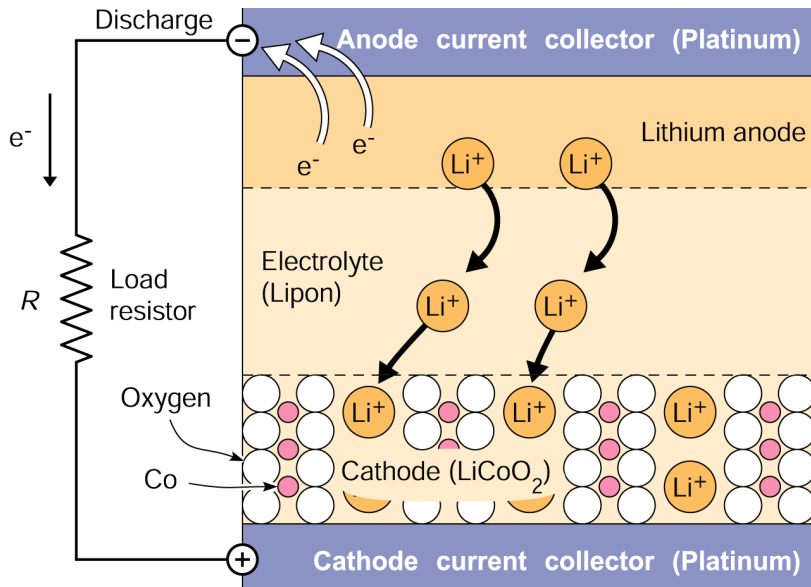
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- ▶ vacancies and excess interstitials
 - still have to cope with virtually ∞ number of inequivalent sites
 - preferred locations based on Li coordination



Li₅P₄O₈N₃: defects

$$E_f = E_{\text{def}} - E_{\text{perf}} - n_{\text{Li}} \mu_{\text{Li}} + q(E_{\text{VBM}} + E_F)$$

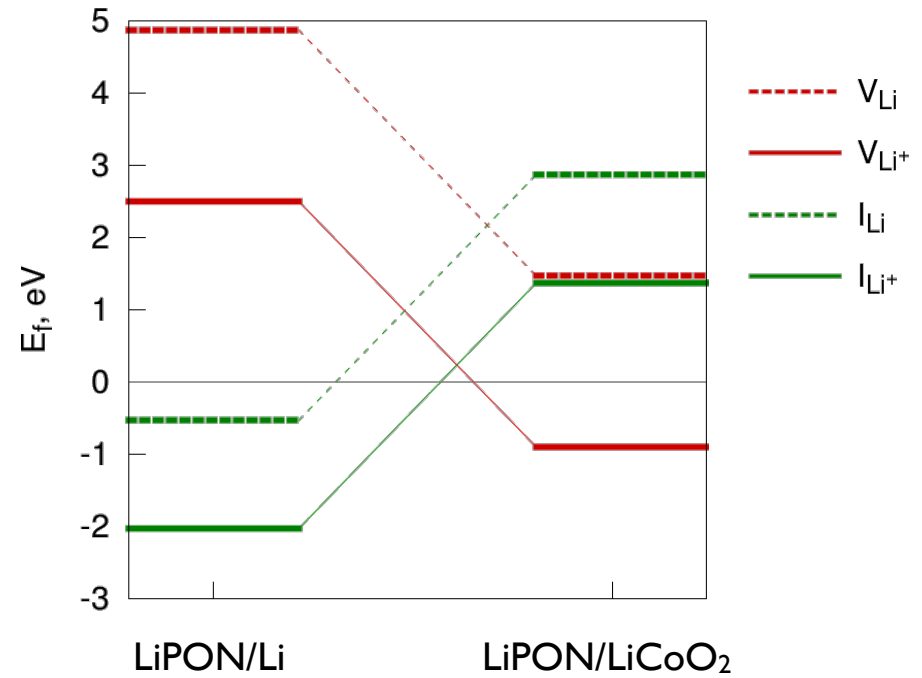
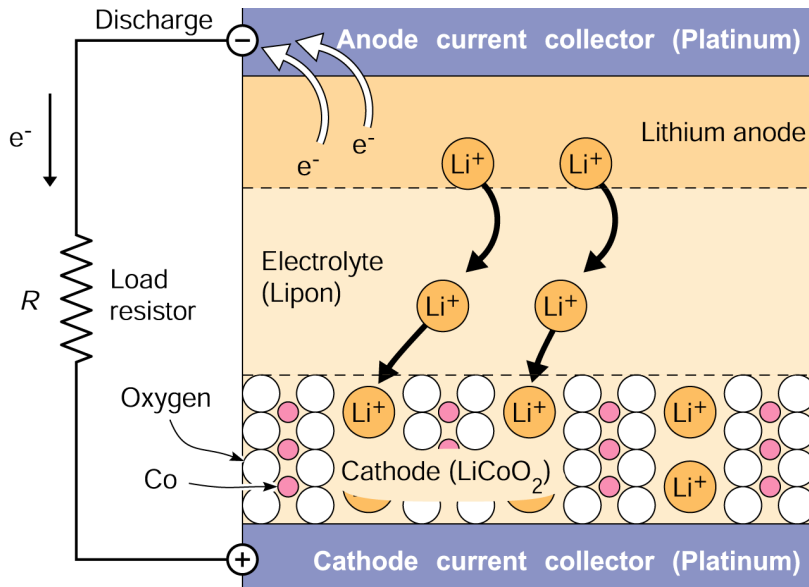
Li reservoir energy: anode Li
 cathode LiCoO₂



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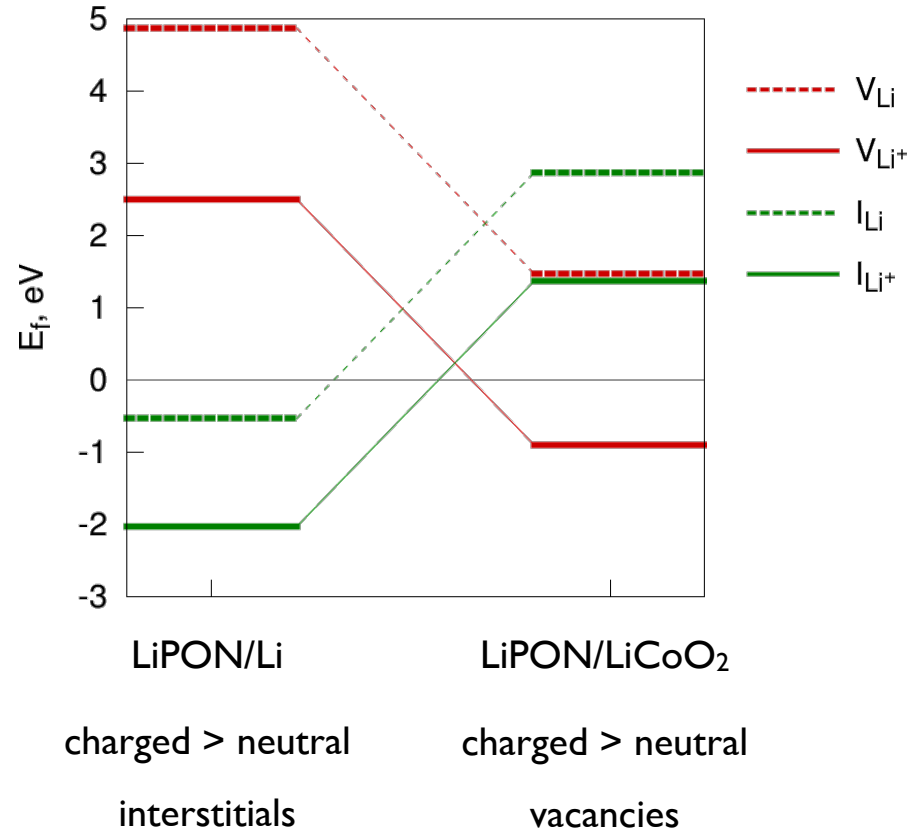
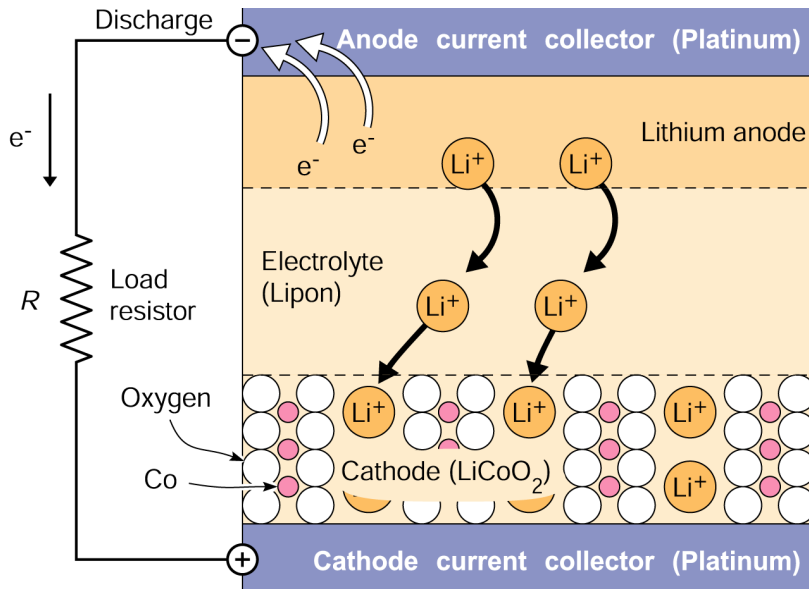
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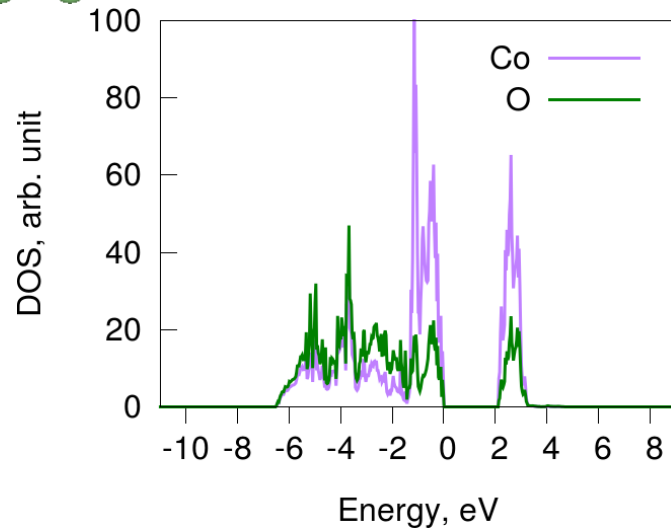
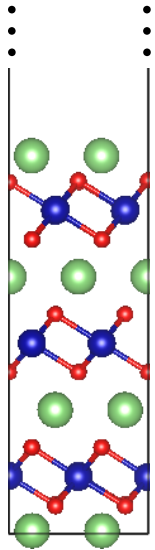
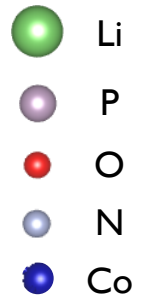
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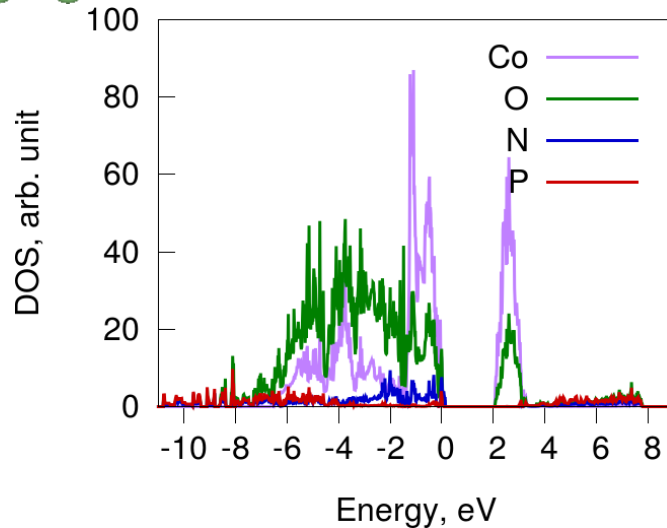
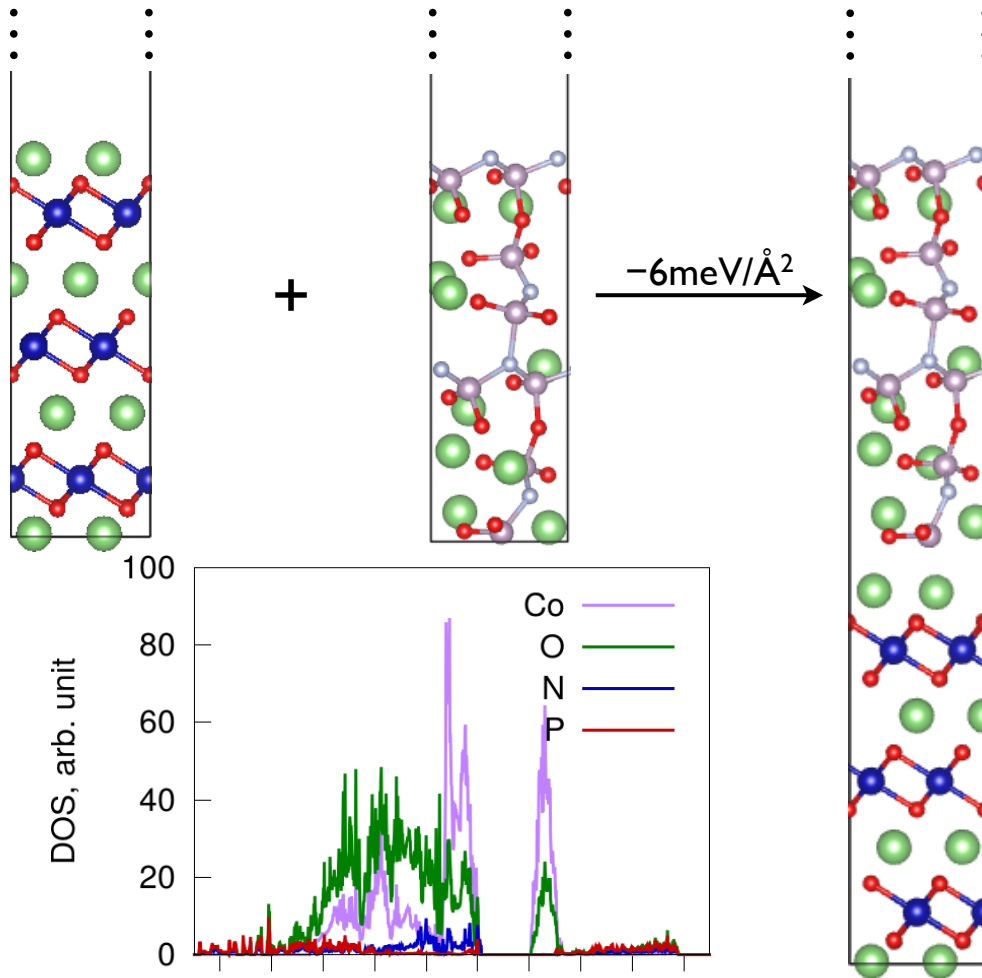
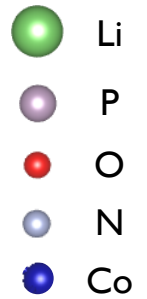
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Interface with LiCoO_2 (0001)



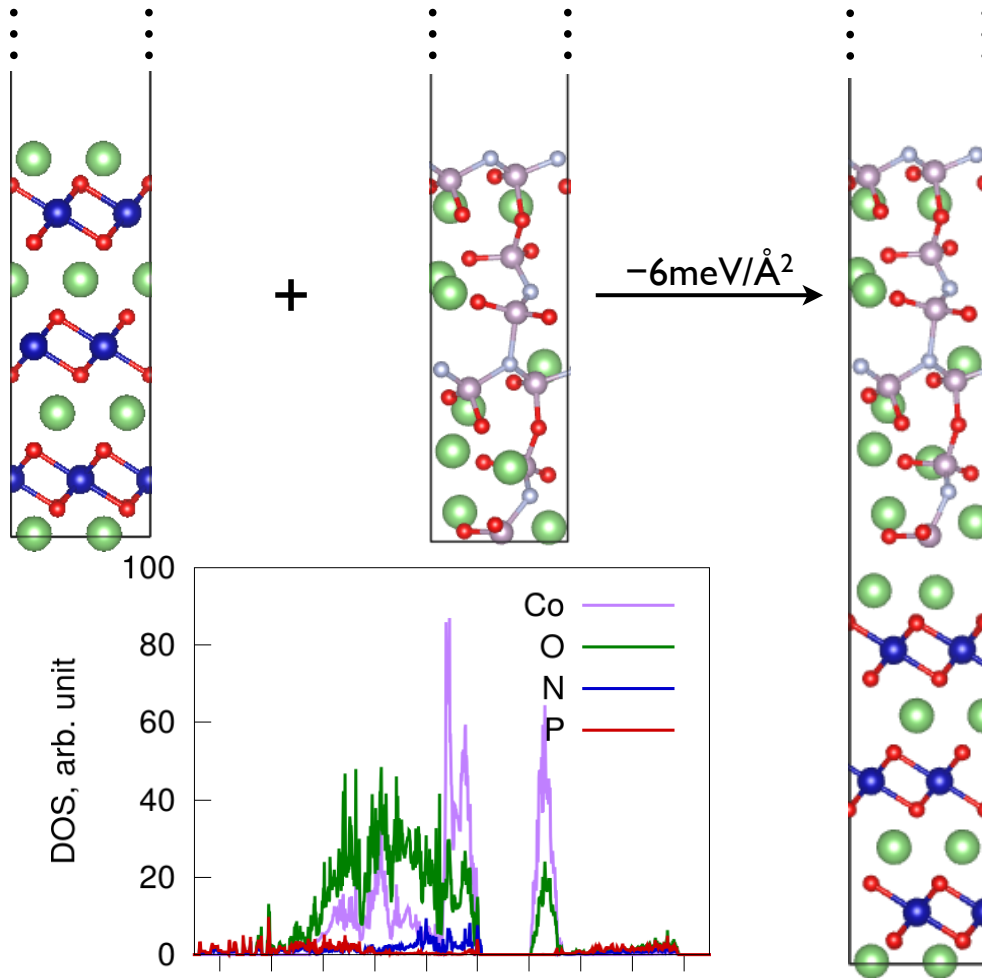
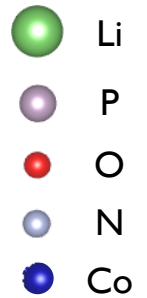
Interface with LiCoO_2 (0001)



- at the interface:
- minor structural relaxation
 - negligible adhesion energy
 - DOS dominated by LiCoO_2

consistent with experiments

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consistent with experiments

- ▶ outlook:
 - $\text{LiPON}/\text{Li}_{1-x}\text{CoO}_2$ interface
 - LiPON/Li interface
 - Li^+ diffusion barriers at interfaces

Acknowledgements



AG Prof. Albe

André Schwöbel & René Hausbrand

you

“The scientist is not a person who gives the right answers, he's one who asks the right questions.

— Claude Lévi-Strauss, *Le Cru et le cuit*, 1964